The kinetics of the partial dehydration of gibbsite to activated alumina in a reactor for pneumatic transport

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The dehidration kinetics of gibbsite to activated alumina was investigated at four different temperatures between 883 K and 943 K in a reactor for pneumatic transport in the dilute two phase flow regime. The first order kinetic behavior of this reaction with respect to the water content of the solid material was proved and an activation energy of 66.5 kJ/mol was calculated. The effect of residence time on the water content is given and compared with theoretical calculations. The water content and other characteristics of the products depend on two main parameters, one is the short residence time and the other is the temperature of the dehydration of gibbsite. The short residence time of the gibbsite particles in a reactor for pneumatic transport prevents crystallization into new phases, as established from XRD analysis data. Reactive amorphous alumina powder, with a specific surface area of 250 m^2/g, suitable as a precursor for catalyst supports is obtained.

Keywords: gibbsite, dehydration kinetics, pneumatic transport, activation energy.

INTRODUCTION

Thermal treatment of gibbsite results in its partial dehydration. Depending on the treatment conditions, products having different properties can be obtained.[1–5] It is already known that the treatment of gibbsite in special regimes, in a reactor for pneumatic transport, *i.e.,* in dilute two-phase flow, makes the obtainment of amorphous intermediate phases with high surface areas, which are more active than starting material, possible.[3,8,9] Due to the latter properties, the activated alumina may be used as a precursor for the preparation of adsorbents and catalysts.

The degree of gibbsite amorphization is affected by its physico-chemical properties and thermal treatment conditions (temperature, reaction medium and residence time).[2,5] In our previous work,[3] the results obtained in a laboratory reactor showed that the degree of

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gibbsite dehydration and amorphization increases within the temperature range from 823 to 923 K. As a consequence of the partial dehydration of the gibbsite, open micro- and mezopores inside the grains of the original gibbsite crystals were formed. Products having a water content smaller than the stoichiometric water content for alumina monohydrate are characterized by a specific surface area greater than 200 m^2/g.

Within this paper, the results of investigations on the kinetics of the partial dehydration of gibbsite, at different temperatures in the range 883 K – 943 K, conducted in a pilot-plant reactor, are presented.

EXPERIMENTAL

Thermal treatment of gibbsite was carried out in the reactor for pneumatic transport, shown in Fig. 1.
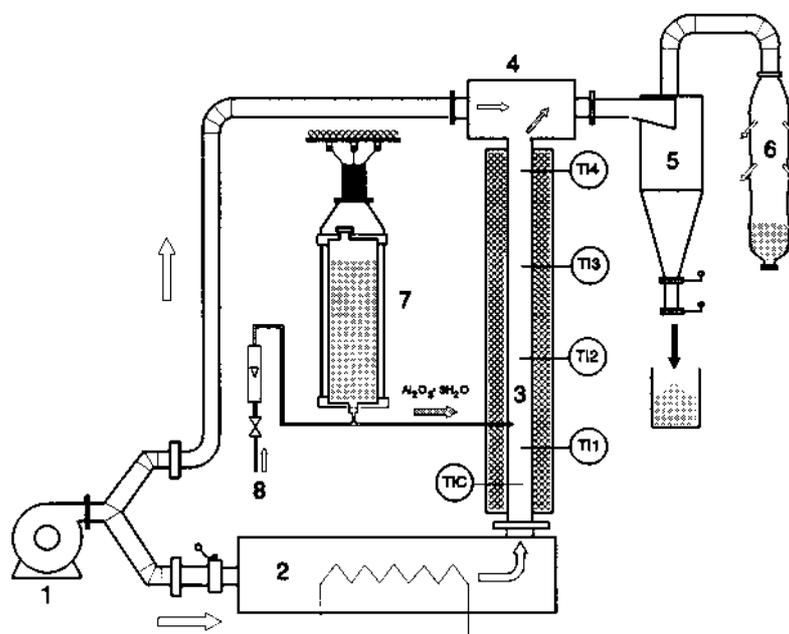

Fig. 1. Schematic diagram of the pilot-scale reactor: 1) blower for air supply, 2) electrical preheaters for air, 3) pneumatic reactor, 4) mixing chamber for warm and cold flow, 5) cyclone, 6) bag filter, 7) vibrating feeding device for gibbsite, 8) compressed air flow for gibbsite transport into the reactor, TIC – temperature inlet controller, TI – thermocouples.

The pilot-scale plant has been designated according to a previous laboratory investigation.[3] It consists of a blower for air supply (1), electric air preheaters (2), a pneumatic transport reactor with a transport tube diameter of 80 mm (3), a mixing chamber for warm and cold air (4), a cyclone (5) and a bag filter (6) for product collection. The gibbsite was introduced into reaction section using a vibrating feeding device (7) and a pneumatic transport line (8) with an air flowrate of 1 m^3/h. In all runs, the gibbsite flowrate was 2 kg/h. Before starting an experiment, the air flow was preheated up to the selected reaction temperature adjusted by a temperature inlet controller (TIC). Along the reactor, four thermocouples (TI1-TI4) were situated in the center of the reactor, which allows the desired tempera-

ture profile within the zone of aluminum oxide trihydrate decomposition to be achieved. With residence time in the heated zone of up to 1s, gibbsite reaches the chosen temperature from 883 K to 943 K. The cold air flow was used for cooling the outlet mixture of air and activated gibbsite (4).

As the starting material, gibbsite, obtained as the intermediate product in the Bayer process (Birač, Zvornik), with a granulation 100 % particles with $d < 10$ m was used. The characteristics of the gibbsite were as follows: water content 2.79 mol H_2O/mol Al_2O_3, bulk density 2.33 g/cm^3 and S_{BET} 4.50 m^2/g. The pore volume, within the range of pore widths from 2 to 50 nm, was 0.02 cm^3/g. The water content of the gibbsite and obtained products were determined by TG analysis.

The specific surface area of the gibbsite and products, S_{BET}, was calculated from the nitrogen adsorption isotherm determined at 77 K in a high vacuum line. The X-ray diffraction analysis (XRD) was performed with a Philips PW 1051 diffractometer, using CuK radiation.

RESULTS AND DISCUSSION

The assumption for both the preliminary laboratory investigations and the design of the pilot-scale plant was that the gibbsite particles have the same linear velocity as the gas in the reactor. In order to verify this assumption, calculations using a model for describing two phase flow were performed. This model is described in detail in our previous papers.[7–9]

The model gives predictions for transport line voids and particle phase velocity, for particles smaller than 1 mm, using the experimental values of the gas velocity and the overall pressure gradient. The results show that the gas phase velocity and particle phase velocity are nearly the same and that the transport line voids are higher than 0.99. Therefore, under the conditions applied in our experiments, there is dilute two phase flow, and the particle residence time in reaction section can be calculated on the basis of measured gas phase velocity. In the course of the thermal activation of gibbsite under the chosen experimental conditions, depending on the time spent in the degradation zone and the activation temperature, flash calcination of the gibbsite into products with a smaller amount of water occurs.

The dependence of the crystalline water content on the residence time at four chosen temperatures is shown in Fig. 2.

The experimental results show that under the selected conditions of temperature and residence time in the heated zone, the gibbsite is partially dehydrated. As expected, the degree of dehydration increases with increasing activation temperature. At the same dehydration temperature, the degree of dehydration increases with increasing particle residence time. This relationship was used to determine the optimum conditions (residence time and activation temperature) to obtain products having the desired properties.

The general first-order reaction equation was used to analyse the experimental data for the dehydration kinetics:

$$\frac{dm}{dt} \quad k(m_0 \quad m) \tag{1}$$

where m is the number of moles of water eliminated per mol of Al_2O_3 at time t, m_0 is the number of moles of initial water per mole of Al_2O_3, and k is the reaction rate constant. Equation (1), can easily be rearranged as follows:
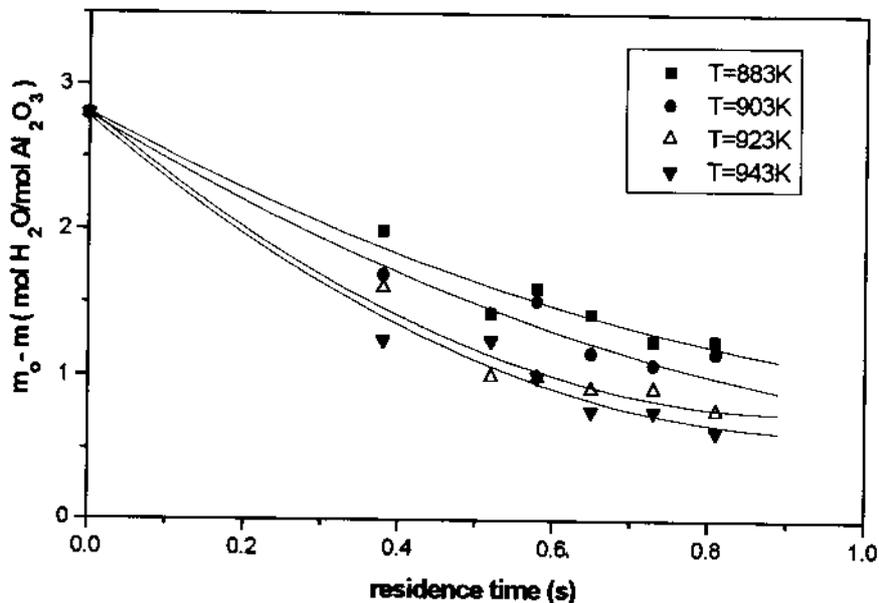
Fig. 2. Water content in the activated samples as a function of particle residence time.

$$\frac{\mathrm{d}m}{m_0 - m} = -k\,\mathrm{d}t \tag{2}$$

$$\ln(m_0 - m) = -kt + \ln m_0 \tag{3}$$

The experimental results according to Eq. (3) are shown in Fig. 3.

The obtained linear dependence between $\ln(m_0 - m)$ and residence time indicates that the dehydration reaction follows first-order kinetics. The rate constants (k), obtained from Fig. 3, were used to calculate the energy of activation from the Arrhenius equation:

$$k = A\,\exp\left(-\frac{E}{RT}\right) \tag{4}$$

The plot of $\ln(k)$ *vs* $1/T$ is shown in Fig. 4.

The dehydration rate constants calculated from the data is found to be as follows:

$$k = 8.85 \times 10^3 \exp\left(-\frac{66.5}{RT}\right) \tag{5}$$

According to Eq. (5), the energy of activation (E) is 66.5 kJ/mol in the temperature range of 883 K to 943 K. The standard deviation of the energy of activation is 0.0416 kJ/mol.

On the basis of Eqs. (3) and (5) for the kinetics of the dehydration of gibbsite in the regime of the pneumatic transport, the water contents of the products activated at a temperature of 913 K, were calculated and the results given in Fig. 5. The theoretical
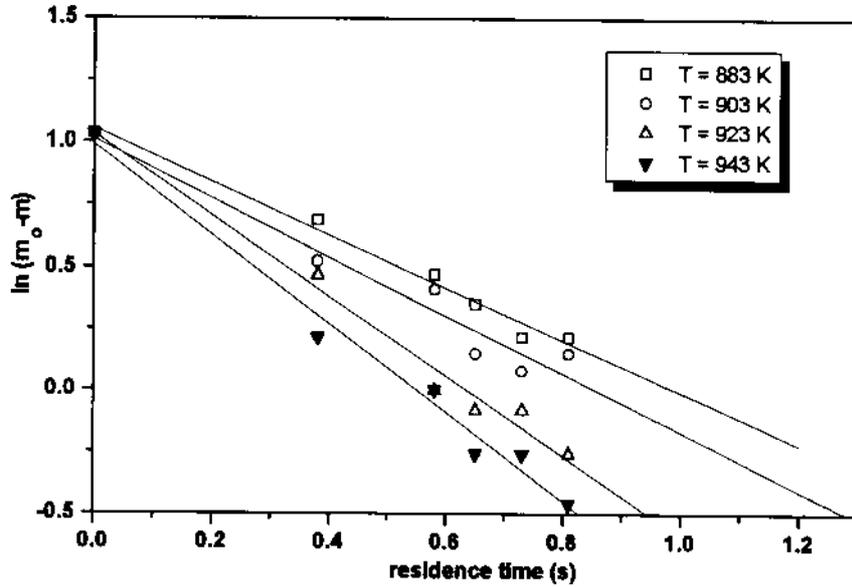
Fig. 3. Linear dependence between ln $(m_0 - m)$ and residence time.

values of the water content of the products are also shown in this Figure for the purpose of comparison.
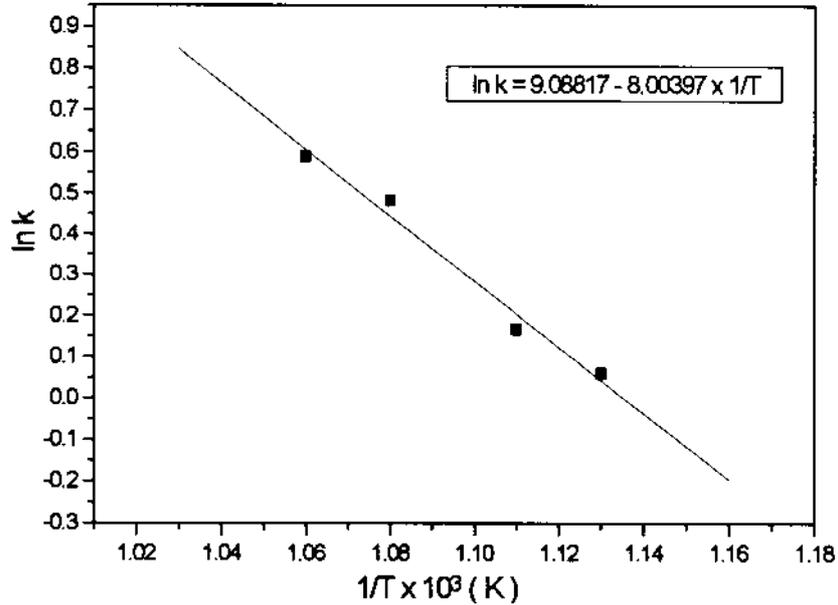

Fig. 4. Arrhenius plot of the dehydration kinetics.

As it can be seen from Fig. 5, the experimental water content values are in good agreement with the theoretical values.
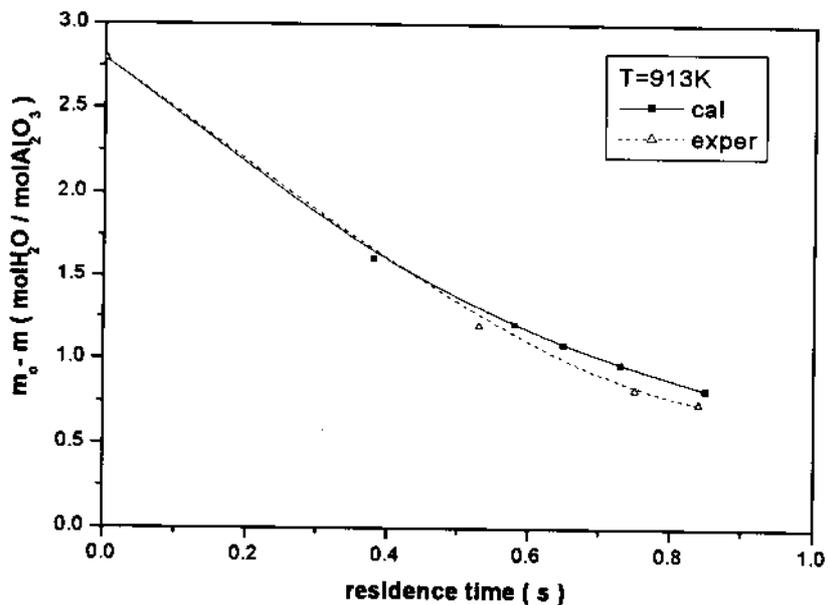
Fig. 5. Variation of the water content of the product with residence time.

The X-ray diffractograms for gibbsite and two activated alumina samples are presented in Fig. 6.

In the X-ray diffractogram of the starting sample, a pure crystal gibbsite phase was identified. The X-ray diffractograms of both the activated alumina samples showed
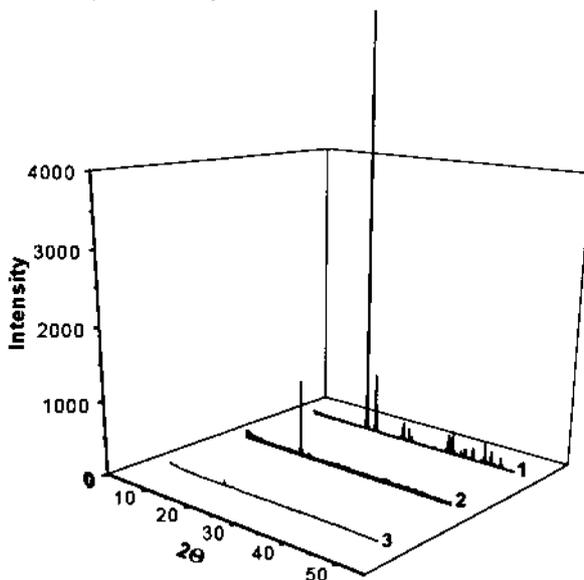

Fig. 6. X-Ray diffraction patterns of gibbsite (1) and the alumina samples activated at 913 K with residence time of 0.53 s (2), and 0.75 s (3).

only the two strongest gibbsite reflections, but with very small intensity. A decrease in the reflection intensity of gibbsite, with increasing residence time was obsereved. The sample obtained at 913 K with a residence time of 0.75 s had a S_{BET} of 250 m^2/g and a pore volume of 0.46 cm^3/g, within the range of pore widths from 2 to 50 nm. The small intensity of the X-ray reflection of this sample, connected with its highly developed surface area, indicated that this alumina is pseudoamorphous.

CONCLUSIONS

The experimental evidence for the partial dehydration of aluminum oxide trihydrate in a reactor for pneumatic transport to activated alumina with a low content of gibbsite, shows that the dehydration folows first-order reaction kinetics with respect to the water content of the solid material.

The temperature dependence of the rate constants for this dehydration can be correlated with the Arrhenius equation, with an activation energy of 66.5 kJ/mol and a frequency factor of 8.85 10^3 s^{-1}.

It is possible to obtain highly active, amorphous alumina, in the pilot-scale plant for the partial dehydration of gibbsite, which can be used, as a precursor for the preparation of adsorbents and catalysts.

И З В О Д

КИНЕТИКА ПАРЦИЈАЛНЕ ДЕХИДРАТАЦИЈЕ ГИБСИТА У РЕАКТОРУ СА ПНЕУМАТСКИМ ТРАНСПОРТОМ

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Кратковремена термичка разградња гибсита је вршена у реактору за пнеуматски транспорт честица на температурама изнад 883 K и времену боравка испод 1 секунде. Добијени активирани прах има висок степен аморфизације и мали проценат полазног гибсита утврђен рендгеноструктурном анализом. Кинетика парцијалне дехидратације гибсита је одређивана у температурном интервалу од 883 K до 943 K. Показано је да је реакција дехидратације гибсита првог реда у односу на садржај воде у чврстом материјалу и израчуната енергија активације износи 66.5 kJ/mol. Одређено је оптимално време боравка честица гибсита и температура дехидратације гибсита у полуиндустријском постројењу, као и утицај температуре активације на садржај воде у активираном продукту.

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